A COURSE OF INSTRUCTION IN THE GENERAL PRINCIPLES OF CHEMISTRY

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CHAPTER I

THE COMPOSITION OF SUBSTANCES

1. Definition of the Field of Chemistry. Its General Principles the Subject of this Course.—*Chemistry* treats of the composition of substances, of their properties in relation to their composition, of changes in their composition, and of the effects attending such changes.

General chemistry, often called also theoretical or physical chemistry, treats of the general principles which have been found to express certain common characteristics of the numerous phenomena of chemistry. To a discussion of the more important of these general principles this Course will be devoted. The divisions of the subject will be taken up in the order in which they were named in the above-given definition of the field of chemistry.

2. Pure Substances and Mixtures, and the Law of Definite Proportions.—Out of the materials occurring in nature there can be prepared substances which, when subjected to suitable processes of *fractionation* (that is, to operations which resolve the materials into parts or fractions), always yield fractions whose properties are identical when measured at the same pressure and temperature. Such substances are called *pure substances;* other substances which can be resolved by such processes into fractions with different properties being called *mixtures.* For example, whether a solid material is a pure substance or mixture may be determined by partially melting or vaporizing it or by partially dissolving it in solvents, and by comparing the value of the density, melting-point, or some other sensitive property, of the unmelted, unvaporized, or undissolved part with that of the original material.

The fundamental idea involved in the preceding considerations is that there exists an order of substances, called pure substances, of relatively great stability toward resolving agencies, each one of which has a perfectly definite set of properties, sharply differentiated from those of other pure substances; so that there is not a continuous series of pure substances whose properties pass over into one another by insensible gradations.

This principle of definiteness of properties in general applies also to the elementary composition of pure substances. This fact is expressed by the *law of definite proportions,* which states that a pure substance, however it be prepared, always contains its elements in exactly the same proportions by weight.

3. The Law of Combining Weights.—To the various elements definite numerical values can be assigned which accurately express the weights of them, or small multiples of the weights of them, which are combined with one another in all pure substances. Such numerical values are called the *combining weights* of the elements. They are essentially relative quantities. Adopting 16 as the combining weight of oxygen, the *combining weight* of any other element may be defined to be that weight of it which combines with 16 parts of oxygen, or with some small multiple or submultiple of 16 parts of oxygen; and the above principle, known as the *law of combining weights,* can be expressed as follows: Elements are present in pure substances only in the proportions of their combining weights or of small multiples of them.

Prob. 1. The oxide of a certain element contains 30.06% of oxygen, and the sulphide of the same element contains 53.46% of sulphur. What does the law of combining weights show as to the relative weights of oxygen and sulphur that may be present in the pure compounds of these two elements?

4. Determination of Combining Weights.—The way in which some important combining weights have been determined is illustrated by the following problem.

Prob. 2. Determine the exact combining weights of silver, potassium, and chlorine from the following data: In a series of eight experiments 801.48 g. of pure potassium chlorate were ignited or treated with hydrochloric acid, yielding 485.66 g. of potassium chloride. In another series of five experiments 24.452 g. of pure potassium chloride were dissolved in water and precipitated with silver nitrate, whereby 47.013 g. of silver chloride were obtained. In a third series of ten experiments 82.669 g. of pure silver were dissolved in nitric acid and precipitated with hydrochloric acid, yielding 109.840 g. of silver chloride.

The combining weights adopted by the International Committee on Atomic Weights for the more important elements are presented in the following table, those multiples being given which have been shown to be the atomic weights, as described in Art. 17. The table is therefore also one of atomic weights.

Aluminum	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Beryllium	Be	9.1
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Calcium	Ca	40.07
Carbon	C	12.005
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Copper	Cu	63.57
Fluorine	F	19.0
Gold	Au	197.2
Helium	He	4.00
Hydrogen	H	1.008
Iodine	I	126.92
Iron	Fe	55.84
Lead	Pb	207.20
Lithium	Li	6.94
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Nickel	Ni	58.68
Nitrogen	N	14.01
Oxygen	O	16.00
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Radium	Ra	226.0
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.06
Thallium	Tl	204.0
Tin	Sn	118.7
Zinc	Zn	65.37

5. **The Atomic and Molecular Theories** account for the fact that elements combine with one another only in the proportions of their combining weights or small multiples of them by assuming that any mass of each element is made up of a very large number of extremely small particles called *atoms;* that these are exactly alike in every respect; that they are not subdivided by chemical processes; that there are as many kinds of atoms as there are elements; that the atoms associate with one another, usually in small numbers, forming a new order of distinct particles called *molecules;* that pure chemical substances are made up of only one kind of molecules, while mixtures contain two or more kinds; and that the molecules of elementary substances consist of atoms of the same kind, those of compound substances of atoms of different kinds.

These assumptions in regard to atoms and molecules have now been confirmed in so many ways that they are no longer hypothetical.

By the above statement *chemical substances* are implicitly defined from the molecular standpoint as pure substances which contain only a single kind of molecule. Thus, the pure substance liquid water contains the two chemical substances whose molecules are H_2O and H_4O_2, these being always present in definite proportions at any definite temperature and pressure, since equilibrium is instantaneously established between them; but the pure substance water-vapor, which contains only molecules of the form H_2O, is a single chemical substance. Pure substances which, like water, water-vapor, and ice, are converted into each other by changes of pressure and temperature, are commonly spoken of as the same substance; but they may consist of different chemical substances, as has been just illustrated.

The relative weights of the atoms of the various elements and of the molecules of the various substances are called their *atomic weights* and *molecular weights,* respectively; and as a standard of reference, the weight of the oxygen atom taken as 16 is adopted.

The atomic theory evidently requires that the weights of elements that combine with one another be proportional to the weights of their atoms or to small multiples of those weights; in other words, that the atomic weights be equal to the combining weights or to small multiples of them. Which multiple of the combining weight is the atomic weight cannot be derived from the elementary composition of substances. It can, however, be derived from other properties, with the aid of certain other principles.

6. Chemical Formulas, Formula-Weights, and Equivalent-Weights.—In order to express the gravimetric composition of compounds, the symbols of the elements are considered to represent their atomic weights and are written in sequence with such integers as subscripts as will make the resulting formula express the proportions by weight of the elements in the compound.

The formula is commonly so written as to represent also the number of atoms of each element present in the molecule, when this has been determined (by any of the methods described in later articles).

The formula represents, in addition, a definite weight of the substance, namely, the weight in grams which is equal to the sum of the numbers represented by the symbols of the elements in the formulas. This weight is called the *formula-weight* of the substance. Thus the formula HNO_3 denotes $1.008 + 14.01 + (3 \times 16.00)$ or 63.02 grams of nitric acid.

Those weights of various substances which enter into chemical reactions with one another are called equivalent weights. Adopting one formula-weight or 1.008 grams of the element hydrogen as the standard of reference, the ***equivalent-weight*** or *one **equivalent*** of any substance is defined to be that weight of it which reacts with this standard weight of hydrogen, or with that weight of any other substance which itself reacts with this standard weight of hydrogen. Thus the equivalent-weight of each of the following substances is that fraction of its formula-weight which is indicated by the coefficient preceding the formula: $\frac{1}{2}Cl_2$; $\frac{1}{4}O_2$; $1Ag$; $\frac{1}{2}Zn$; $\frac{1}{3}Bi$; $1NaOH$; $\frac{1}{2}Ba(OH)_2$; $\frac{1}{2}H_2SO_4$; $\frac{1}{3}H_3PO_4$; $\frac{1}{3}AlCl_3$; $\frac{1}{4}K_4Fe(CN)_6$. The equivalent-weight of a substance may have different values depending on whether it is considered with reference to a reaction of metathesis or to one of oxidation and reduction. Thus, the metathetical equivalent of ferric chloride is $\frac{1}{3}FeCl_3$, but its oxidation-equivalent (with respect to its conversion to ferrous chloride) is $1FeCl_3$; the metathetical equivalent of potassium chlorate is $1KClO_3$, but its oxidation-equivalent (with reference to its reduction to KCl) is $\frac{1}{6}KClO_3$.